MATHEMATICAL PROBLEMS IN MICO-MECHANICS AND COMPOSITE MATERIALS

Final Technical Report

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FINAL TECHNICAL REPORT FOR ARO CONTRACT DAAL03-92-G-0011

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ABSTRACT

This is the final technical report on ARO contract DAAL03-92-G-0011, which began February 1, 1992 and ended January 31, 1995. The scientific focus of this project lies at the frontier where mathematics meets materials science. We are concerned with the effective moduli of composites, the formation of microstructure in coherent phase transitions, and random solutions of nonlinear evolution equations. These diverse problems are linked by a common theme: the relationship between microstructure and macroscopic behavior. Our achievements under this contract include: (i) development of a theory for how symmetry and texture determine the recoverable strain of a shape-memory polycrystal; (ii) development of a model for piezoceramic composites, providing insight toward the design of such materials for use in sensors or actuators; and (iii) new, optimal bounds on the effective behavior of elastic polycrystals. The training of young scientists has been a major part of our activity.

CONTENTS

1. INTRODUCTION

This is the final technical report on ARO contract DAAL03-92-G-0011, which began February 1, 1992 and ended January 31, 1995. The scientific focus of this project lies at the frontier where mathematics meets materials science. We are concerned with the effective moduli of composites, the formation of microstructure in coherent phase transitions, and random solutions of nonlinear evolution equations. These diverse problems are linked by a common theme: the relationship between microstructure and macroscopic behavior. The relevant mathematical tools include homogenization, the calculus of variations, and the theory of stochastic processes.

The scope of this effort is rather broad. One type of goal involves composites with advantageous or even extremal effective behavior. Projects in this class include understanding the shapes of coherent precipitates (Kohn, with Grabovsky and Lu -- Section 2.2.2); finding optimal bounds for the effective moduli of elastic polycrystals (Avellaneda and Milton, with Gibiansky, Cherkaev, and Rudelson -- Section 2.1.2); and designing piezoceramic composites with strong electromechanical coupling (Avellaneda and Swart -- Section 2.1.3). A second type of goal involves the mechanics of smart materials. Projects in this class include modelling the "rubber-like" behavior displayed by certain shape-memory alloys in the martensitic phase (Bhattacharya and Swart, with James -- Section 2.3.2), and the analysis of shape-memory polycrystals (Bhattacharya and Kohn -- Section 2.3.1). A third type of goal is to understand random solutions of nonlinear evolution equations. Such problems arise in several areas of statistical physics (Avellaneda and Ryan, with E -- Section 2.4.2).

The mentoring of postdocs is a major part of our activity. This contract supported postdoctoral researchers K. Bhattacharya (spring 1992 and academic year 1992-3); Elliott Alber (partial support, academic year 1993-4); Nick Firoozye (partial support, academic year 1993-4) and Pieter Swart (fall 1995). About 3/4 of the contract's funding was spent on postdoc salary, including associated fringe benefits and overhead. Our postdocs have done very well in the job market: Bhattacharya is now an Assistant Professor at Caltech (Division of Engineering and Applied Science); Alber holds a postdoctoral position at Lawrence Livermore Laboratory (the group led by M. Baskes); Firoozye is an Assistant Professor at the University of Illinois -- Champaign/Urbana (Mathematics); and Swart will join Los Alamos National Laboratory in June, 1995 (Mathematical Modelling group, Theory Division). We have worked closely with other CIMS postdocs too, including Y. Achdou, J. Helsing, and J.-F. Clouet.

We are also active in the training of students. We supervised the thesis research of 5 Ph.D. students who finished their degrees during 1992, 1993, or 1994. Another 4 students are presently working with us in areas related to this contract. Their work is summarized in Section 3. This contract did not provide academic year support for these students, but it did provide summer support for Yury Grabovsky (1992-4), Chris Apelian (1993), Reade Ryan (1993), and Weimin Jin (1994). Apelian and Ryan received academic-year support from an affiliated AASERT contract.

We are particularly proud of several recent students who have won prizes for their thesis research: Tami Olson won New York University's 1992 Sokol Prize (worth 10,000 dollars); Pedro Girao won SIAM's 1993 Student Paper Contest; Karen Clark won the Courant Institute's 1993 Sandra Bleistein award; and Yury Grabovsky won both the New York Academy of Science's 1994 Minoru and Ethel Tsutsui Award (worth 1500 dollars) and the Courant Institute's 1995 Wilhelm T. Magnus award.

For an interdisciplinary effort such as ours to succeed, contact with scientists from the relevant application areas is of paramount importance. Therefore we often attend (and sometimes organize) conferences at the interface between mathematics and mechanics. Here is a selective list for 1994 alone: SPIE Conference on Smart Materials, 2/94 (Avellaneda); SIAM Meeting on Applied Mathematics and Computation in Materials Science, Pittsburgh, 3/94 (Avellaneda, Kohn, and Milton); ONR Transducer Workshop, Penn State, 4/94 (Avellaneda); ARO Workshop on Computer Synthesis of Structure of Advanced Composites, Moscow, 5/94 (Kohn); US National Congress on Theoretical and Applied Mechanics, 6/94 (Kohn), Society for Engineering Science, College Station, 10/94 (Avellaneda, Kohn, Milton), ASME Winter Meeting 11/94 (Avellaneda). Avellaneda was on the organizing committee for the SPIE meeting; Kohn was on the organizing committee for the SIAM meeting, and organized several special sessions at the SES meeting. Milton is on the organizing committee for IMA's 1995-6 special year on Mathematics in Materials Science.

Our ARO-sponsored work is continuing under a new contract, DAAH04-95-1-0100, which began March 1, 1995. Related work is also being funded by NSF.

2. MAJOR RESEARCH ACCOMPLISHMENTS

2.1. COMPOSITE MATERIALS

A composite material is by definition a mixture of homogeneous continua on a length scale small compared to the loads and boundary conditions, but large enough for continuum theory to apply. Its *effective moduli* describe its overall or macroscopic behavior. Different types of physical behavior lead to different notions of effective moduli. For example, the effective conductivity is a real-valued, second-order tensor relating a (direct current) electric field to the associated current flux; the effective Hooke's law is a fourth-order tensor relating stress and strain; and the effective permittivity is a complex-valued, second-order tensor describing the refractive and absorptive response of a composite to electromagnetic radiation, when the wavelength is much greater than the length scale of the microstructure.

Our research in this area has diverse goals. One is the search for microstructures with advantageous physical properties. Another is the derivation of geometry-independent bounds -- an essential tool in the search for extremal microstructures, since they express limitations on what can be achieved. Our work includes a broad variety of applications, ranging from phase transformations (the shapes of coherent precipitates) to remote sensing (the design of piezoceramic composites for use in sensors and actuators). We

also seek a deeper understanding of the "structural" aspects of the subject: for example, how should the various new techniques for proving bounds be used to maximum advantage?

2.1.1. Fundamentals

(a) K. Clark and G. Milton, "Modelling the effective conductivity function of an arbitrary two-dimensional polycrystal using sequential laminates," Proc. Royal Society Edinburgh 124A (1994) 757-783.

(b) G. Francfort and G. Milton, Sets of conductivity and elasticity tensors stable under lamination," Comm. Pure Appl. Math. 47 (1994) 257-279.

(c) G. Milton, "A link between sets of tensors stable under lamination and quasiconvexity," Comm. Pure Appl. Math. 47 (1994) 959-1003.

The construction known as *sequential lamination* has been very successful in providing examples of composites with extremal effective behavior. We have as yet no general understanding of why it works so well. Milton's paper (a), with Clark, provides a partial explanation. Its main result is that "sequential lamination generates all possible effective conductivity functions of two-dimensional polycrystals." To explain what this means, recall that a polycrystal is a composite made by mixing a single, anisotropic material with itself in different orientations. The (tensor-valued) effective conductivity σ_* depends on the principal conductivities σ_1, σ_2 of the basic crystal, and also on the microstructure. Thus the microstructure can be viewed as determining the *effective conductivity function* $\sigma_*(\sigma_1, \sigma_2)$. The work of Clark and Milton identifies the precise class of functions that can arise this way, and shows that each can be achieved as the effective conductivity function of a (possibly infinite-rank) sequential laminate.

Milton is also pursuing another program for exploring the adequacy of sequential lamination. The essential idea is as follows. Starting from any set U of components we may consider the set of all composites LU that can be made from them by sequential lamination. By its very definition, this set is closed under the formation of layered composites. If we could show it was closed under the formation of composites with arbitary microstructure, then we would be done: LU would be the set of *all* composites (sometimes known as the G-closure, GU) achievable by mixing components from U. The first step in implementing this program was the paper (b), joint with G. Francfort, which explores the properties of lamination-closed sets. The second step was the paper (c), which gives a general connection between lamination-closed sets and bounds on effective moduli. The third step -- not yet complete -- will be to sharpen the bounds in (c), since in their present form they do not yet suffice to show that lamination-closed sets are G-closed. It should be mentioned that the equivalence of G-closure and lamination-closure is by no means certain. Sverak's recent paper [1] shows that sequential lamination does not always suffice for the closely related task of relaxing nonconvex variational problems.

2.1.2. Bounds on effective moduli

(a) G. Allaire and R. Kohn, "Optimal lower bounds on the elastic energy of a composite made from two non-well-ordered isotropic materials," Quart. Appl. Math. 52 (1994) 311-333.

(b) L. Gibiansky and G. Milton, "On the effective viscoelastic moduli of two-phase media: I. Rigorous bounds on the complex bulk modulus," Proc. Roy. Soc. London 440A (1993) 163-188.

(c) K. Clark and G. Milton, "Optimal bounds correlating electric, magnetic, and thermal properties of two-phase, two-dimensional composites," to appear in Proc. Roy. Soc. London Ser. A.

(d) G. Milton and A. Movchan, "A correspondence between plane elasticity and the two-dimensional real and complex dielectric equations in anisotropic media," submitted to Proc. Roy. Soc. London Ser. A.

(e) M. Avellaneda, A. Cherkaev, L. Gibiansky, G. Milton, and M. Rudelson, "A complete characterization of the possible bulk and shear moduli of planar crystals," submitted to J. Mech. Phys. Solids.

The paper (a) by Kohn and Allaire is concerned with optimal bounds for the elastic energy of a two-component composite. These may be viewed as extensions of the well-known Hashin-Shtrikman bounds on the effective bulk and shear moduli of an isotropic elastic composite. When the component materials are "well-ordered" we know a great deal, see e.g. [2-4]. When the component materials are not well-ordered, however, we know much less. Walpole found the optimal bounds on the effective bulk modulus [5]. The new work of Allaire and Kohn extends Walpole's result, obtaining an optimal lower bound on the elastic energy at any fixed strain. This result is proved in two different ways -- once by the translation method, and once by a variant of the Hashin-Shtrikman-Walpole variational principle.

The paper (b) of Milton and Gibiansky considers viscoelastic composites. When the loading is periodic (with a wavelength that is large compared to the length scale of the microstructure), such composites can be described by complex-valued Hooke's laws. The main result of (b) is a viscoelastic analogue of the well-known Hashin-Shtrikman bounds on the effective bulk modulus. Such bounds bracket the response of the composite to the propogation of acoustic waves. The analysis in (b) shows that the effective complex bulk modulus must lie in a lens shaped region of the complex plane. Moreover special points on the boundary of the lens can be identified with specific geometries. These geometries exhibit extreme viscoelastic response and are natural candidates for consideration when the objective is to optimize the vibrational response of a composite. This paper offers the first specific application of a new variational principle for complex effective moduli, which was formulated a few years ago by Cherkaev, Gibiansky, and Milton [3,6].

The paper (c) by Milton and Clark derives new bounds coupling the effective electric, magnetic, and thermal properties of a two-phase composite in two space dimensions. Such results are potentially of practical importance, since they permit one to estimate a certain effective property (e.g. thermal conductivity) by measuring physically different ones (e.g. electric and magnetic). Mathematically, this problem is concerned with the effective tensor σ_*, viewed as a function of the tensors σ_1, σ_2 which represent the

properties of the two component materials. The work of Milton and Clark gives an algorithm for identifying the exact set of possible values of $\sigma_*(\sigma_1,\sigma_2)$ given knowledge of this function at two or more specified points (i.e. given $\sigma_*(\sigma'_1,\sigma'_2)$ and $\sigma_*(\sigma''_1,\sigma''_2)$, in case just two points are specified). This can be viewed as a tensorial extension of scalar results due to Bergman, Golden, and Milton [7-8]. Alternatively, it can be viewed as an extension of the recent results by Cherkaev and Gibiansky concerning bounds coupling two effective properties [9]. The method of Clark and Milton is quite different from those of the papers just cited, but it is in some sense a tensorial extension of [8].

The paper (d) by Milton and Movchan gives an exact correspondence between certain problems of two-dimensional elasticity and associated two-dimensional complex dielectric problems. Equivalently the paper provides an exact correspondence between plain-strain elasticity and antiplane-strain elasticity. These correspondences extend to composite materials and imply relations between effective elastic moduli and effective dielectric moduli. In a two-phase composite the moduli of the phases must satisfy certain relations for the correspondences to hold (in particular at least one phase must be anisotropic). However the geometry of the phases can be completely arbitrary. As such the relation will provide a useful benchmark for testing approximation schemes and numerical simulations.

The paper (e), a joint project of Milton, Avellaneda, Cherkaev, Gibiansky, and Rudelson, proves new, optimal bounds for the effective elastic behavior of a macroscopically isotropic two-dimensional polycrystal. It is notable both for its methods and for its results. Regarding methods, it is among the first applications of the ''translation method'' to elastic polycrystals. Interestingly, the successful translation is not a function of strains alone -- it also depends on the infinitesimal rotations. Another methodological point: the optimal microstructures were initially found by searching the space of sequential laminates numerically; then, once the right answers were known, the authors found analytical proofs of their optimality. Regarding results: for some special classes of crystals -- in particular those with ''square symmetry'' -- the upper and lower bounds coincide, producing an exact formula for the effective behavior. Such exact formulas are useful, among other reasons, for testing mean field theories and approximate formulas found in the engineering literature.

2.1.3. Composites for use in sensors and actuators

(a) M. Avellaneda and G. Harshe, "Magnetoelectric effect in piezoelectric + magnetostrictive multilayer (2-2) composites," J. Intell. Mater. Struct. 5 (1994)

(b) M. Avellaneda and T. Olson, "Effective medium theories and effective electromechanical coupling factors of piezoelectric composites," J. Intell. Mater. Struct. 4 (1993) 82-88.

(c) P. Swart and M. Avellaneda, "The role of matrix porosity and Poisson's ratio in the design of high-sensitivity piezocomposite transducers," in Adaptive Structures and Composite Materials: Analysis and Applications, E. Garcia, H. Cudney, and A. Dasgupta, eds., AD-Vol. 45, ASME, 1994.

(d) M. Avellaneda and P. Swart, "Calculating the hydrostatic performance of 1-3 composite piezoceramic materials," submitted to J. Acoust. Soc. Amer.

Transducers convert one type of energy to another -- for example, elastic waves to electrical signals. To make such devices one requires materials with strong cross-field coupling. Suitably designed composites often work better than any single naturally-occurring materials. Avellaneda has been exploring this topic for several years, initially with T. Olson and G. Harshe, more recently in collaboration with P. Swart.

The paper (a) with Harshe addresses magnetoelectric coupling. Such kind of coupling is not found in homogeneous materials, except at extremely low temperatures of a few degrees Kelvin. But one can nevertheless create a magnetoelectric *composite* by layering a piezoelectric material with a magnetostrictive one. Avellaneda and Harshe show how to evaluate the effective properties of such a composite. Then they apply their method to calculate a theoretical "figure of merit" when the component materials are PZT and Terfenol-D.

The paper (b) with Olson addresses piezoelectric composites. Its main results are (i) a formula for the effective behavior when the microstructure is layered; (ii) a mean field theory for the effective behavior when the microstructure is polycrystalline; and (iii) a geometry-independent bound on the electromechanical coupling of a piezoelectric composite.

The more recent work (c)-(d) by Avellaneda and Swart is also concerned with piezoelectric composites, however it makes closer contact with the materials science literature. Their attention is on "1-3 piezoceramic composites," i.e. materials made by embedding piezoceramic rods in a soft, polymer matrix. The 1-3 microstructure has been shown experimentally to reduce the transverse piezoelectric coupling while maintaining a large longitudinal coupling factor, thereby increasing the overall acoustic sensitivity relative to transducers made of pure ceramic. In the past, these materials have mainly been assessed and improved by building prototypes. Avellaneda and Swart have developed an alternative, analytical approach, which captures the complicated dependence of the effective behavior upon the physical properties of the components and the volume fraction of the rods. The first key step was to show that the response of such a composite depends on the microstructure only through a few "geometrical parameters," each having a simple (purely mechanical) interpretation. The second key step was to evaluate these geometrical parameters by means of a differential effective medium theory. The outcome is a virtually explicit representation for the effective behavior. Optimization no longer requires building a sequence of prototypes; now it can be done on a workstation instead. This analysis has also led to qualitative insight. In the typical high-contrast case (when the matrix is much softer than the piezoceramic inclusions) the critical parameter turns out to be the Poisson's ratio of the matrix.

2.1.4. Special microstructures

(a) Y. Grabovsky and R. Kohn, "New microstructures minimizing the energy of a two phase composite in two space dimensions. I: the confocal ellipse construction," to appear in J. Mech. Phys. Solids.

(b) Y. Grabovsky and R. Kohn, "New microstructures minimizing the energy of a two phase composite in two space dimensions. II: the Vigdergauz microstructure," to appear in J. Mech. Phys. Solids.

(c) N. Nicorovici, R. McPhedran, and G. Milton, "Optical and dielectric properties of partially resonant composites," Phys. Rev. B 49 (1994) 8479-8482.

Papers (a) and (b) emerged from the thesis research of Yury Grabovsky. They address ''elastically extremal'' composites, for example those which mix two isotropic elastic materials so as to minimize the effective energy $< A_*\xi,\xi >$ at a given strain ξ. We have known for years how to identify the extreme value of the energy, and how to obtain extremal microstructures by sequential lamination. But if the hydrostatic part of ξ is large compared to the deviatoric part then sequential lamination is not the only possibility. The work of Grabovsky and Kohn examines in detail two attractive alternatives. One is the ''Vigdergauz microstructure,'' which consists of a periodic array of properly-shaped holes [10]. The other is the ''confocal ellipse microstructure,'' which packs space with scaled copies of a coated ellipse. The papers listed here are restricted to 2D elasticity and isotropic component materials, however Grabovsky's thesis also considered 3D elasticity and anisotropic components.

The paper (c) by Milton, Nicorovici, and McPhedran explores a new type of resonance, concentrating for specificity on a specific 2D microstructure -- the coated cylinder geometry. Usually resonances are associated with a global increase in field magnitude, but the type of resonance reported in (c) is localized in a zone near the coated cylinder surface, where the field exhibits wild spatial oscillations. This might provide a mechanism for surface-enhanced Raman Scattering, which is believed to be due to the presence of large electromagnetic fields near surfaces. Surprisingly, the field far from the cylinder surface is close to that one would get by subsituting the coated cylinder with an "equivalent" solid one -- and this equivalence holds regardless of the form of the exterior field. An interesting consequence arises when the "equivalent" cylinders percolate: then the associated critical exponents also describe the behavior of a dilute suspension of coated cylinders!

It was long an open question whether all "reasonable" materials must have positive Poisson's ratio. It was known that one could design "foams" or "networks" with negative Poisson's ratio, and that such structures have interesting applications [11]; but many people believed thought such behavior could not be achieved by mixing two continua with positive Poisson's ratio. Milton's paper [12] showed otherwise. He has recently gone further, showing in collaboration with A. Cherkaev that positivity is the *only* restriction on the tensor of effective moduli. In other words, if a fourth order tensor A with the symmetries of a Hooke's law defines a positive definite quadratic form on strains, then A can be realized as the effective

tensor of a mixture of two isotropic elastic materials, one sufficiently compliant and the other sufficiently rigid.

2.1.5. Structural optimization

(a) G. Allaire and R. Kohn, "Optimal design for minimum weight and compliance in plane stress using extremal microstructures," Eur. J. Mech. A/Solids 12 (1993) 839-878

The goal of structural optimization is to choose the shape or composition of a structure so as to optimize some feature of its mechanical response. This paper by Kohn and Allaire is the culmination of several years' work in this area. Its focus is the shape optimization of two-dimensional elastic structures in plane stress, with compliance and weight as design criteria. A relaxed formulation is used, whereby perforated composites are permitted as structural components. The optimal composite is determined analytically at each point in terms of the local stress field, by making use of Hashin-Shtrikman-type bounds. This reduces the optimal design problem to a (nonconvex but well-posed) minimization over the space of statically admissible stress fields -- equivalent to a special problem of geometrically linear but physically nonlinear elastostatics. Allaire and Kohn solve this problem numerically, using a finite element discretization, for a variety of different loading conditions.

We are delighted to report that homogenization-based methods for structural optimization are becoming increasingly popular with the mechanical engineering community, see e.g. [13-14]. A homogenization-based optimization code marketed by Kikuchi and his collaborators is presently in use as a research tool at several major automobile companies. A group at the University of Michigan has begun to explore the manufacture of sequentially laminated composites by means of rapid-prototyping technologies [15].

2.1.6. Geophysical applications

(a) Y. Achdou and M. Avellaneda, "Influence of pore roughness and pore- size dispersion in estimating the permeability of a porous medium from electrical measurements," Phys. of Fluids 4A (1992) 2651-2673.

Avellaneda's work with Achdou addresses the relation between the "dynamic effective permeability" $k(\omega)$ of a porous medium and the "formation factor" F. The dynamic effective permeability measures the response of the medium to a periodic pressure gradient; at frequency 0 it is just the constant in D'Arcy's law. The formation factor is the effective conductivity of the same microstructure, when the pores are filled with a fluid of unit conductivity and the solid is treated as a perfect insulator. Relations between the two are important, because it is easier in practice to make electrical measurements than to measure permeability. There is considerable empirical and analytical evidence that these quantities

should be coupled, and that the functional form of $k(\omega)$ is in a certain sense "universal" [16-17]. Avellaneda and Torquato have obtained rigorous results of this type, but only for microstructures which are sufficiently smooth. The work of Achdou and Avellaneda shows, by direct numerical simulation, that microstructures with rough pores or high tortuosity depart significantly from the proposed "universal" behavior.

2.1.7. Structured interfaces

(a) E. Alber and R. Kohn, "Effective boundary conditions at structured interfaces," in preparation.

Most of our work on composites treats the material interfaces as being "perfectly bonded." But real interfaces often have structure. When two solids are bonded adhesively the "glue" can be represented as a thin interphase layer. A rather different example is the case of a "functionally gradient material," whose properties vary smoothly across a thin transition region rather than change abruptly at a sharp interface.

The work of Alber and Kohn considers the simplest example of a structured interface: a pair of elastic bodies separated by a thin elastic layer of thickness h. Their attention is on the asymptotic behavior as $h \to 0$ with the elastic moduli held fixed. This problem can be addressed using the two scale method, as Panasenko showed some years ago [18]. Two alternative approaches have recently been developed in the mechanics literature: one by Bovick, Bostrom, and Olsson, based on "analytic continuation" [19,20]; and another by Wickham, based on a boundary integral formulation [21]. The paper (a) by Alber and Kohn will compare and contrast these different approaches.

2.2. PHASE TRANSFORMATIONS

Coherent phase transformations of crystalline solids lead to mixtures of distinct phases or phase variants with characteristic fine scale structures. Such transformations can be modelled using continuum elasticity. The microstructures arise due to elastic energy minimization, so this topic is closely linked to the identification of extremal composites. One application area is martensitic phase transformation. Another is coherent precipitation. We are also interested in fundamental issues, such as how to relax non-convex energies, and how to characterize Young measure limits of gradients.

2.2.1. Microstructure and energy minimization

(a) K. Bhattacharya, "Comparison of the geometrically nonlinear and linear theories of martensitic transformation," Cont. Mech. Thermodyn. 5 (1993) 205-242.

(b) K. Bhattacharya, N. Firoozye, R. James, and R. Kohn, "Restrictions on microstructure," Proc. Roy. Soc. Edinburgh 124A (1994) 843-878.

Ball and James have developed an approach to modelling martensitic phase transitions based on (geometrically) nonlinear elasticity e.g. [23]. A similar approach using geometrically linear elasticity had previously been explored in the metallurgical literature by A. Khachaturyan and A. Roytburd e.g. [22]. Bhattacharya's paper (a) provides a systematic comparison of these two approaches. For some purposes -- e.g. for predicting the orientations of twin planes -- the two are very similar. For other purposes -- e.g. for modelling the wedge-like microstructure that occurs in many shape-memory materials -- the nonlinear theory works well and the linear approach is simply inadequate. In still other contexts -- e.g. finding self-accommodating microstructures that mix several variants of martensite -- the linear theory admits a complete solution while the nonlinear approach appears utterly intractable. The right goal, of course, is not to decide which theory is "better." Rather, we must learn the power and limitations of both approaches, and how to apply them together to maximum effect.

Paper (b) addresses the question: what does it mean for several phases to be elastically compatible? In other words, when can several elastic phases with different stress-free strains participate coherently in an essentially stress-free microstructure? If there are only two phases the answer is well-known: the phases are compatible if and only if they can be layered together in a stress-free manner. But the general case is much more complex. It turns out that three elastic phases can be pairwise incompatible and yet mutually compatible. There is even an example involving three of the six variants produced by a type of cubic to orthorhombic phase transformation. Related work has been done by Kinderlehrer, Matos, Pedregal, Sverak, and Tartar, much of it published in the conference proceedings volume [24]; the introduction of (b) summarizes the state of the art.

2.2.2. Application to coherent precipitates

(a) R. Kohn and J. Lu, "Elastic energy minimization and the shapes of coherent precipitates," in preparation.

This was Jiangbo Lu's thesis project. When precipitates form coherently in a crystalline solid, they take on a characteristic shape, often plate-like but sometimes spherical or even cuboidal. There is an extensive metallurgical literature aimed at explaining these morphologies via elastic energy minimization. However, virtually all this literature assumes either (i) that the precipitates are ellipsoids, at sufficiently low volume fraction that multi-particle interactions can be ignored (e.g. [25,26]) or else (ii) that the matrix and precipitate phases have the same Hooke's law tensor (e.g. [22]).

Now there is a new approach, based on methods developed for identifying composites with extremal effective behavior. This approach makes no hypothesis about particle shape or volume fraction, and it permits the two phases to have different Hooke's laws. The work of Kohn and Lu explores the consequences of this approach in a two dimensional (plane strain) setting, when both the matrix and the precipitates have isotropic Hooke's laws. No restriction is placed on the mismatch strain. There are basically

two regimes. In the first, elastic energy minimization implies a layered (plate-like) morphology. In the second, elastic energy minimization is consistent with a multitude of different, more complex morphologies. Scientifically speaking, the degeneracy of the second regime is the most important conclusion. In this case elastic energy minimization alone gives an ambiguous prediction, so surface energy and elastic anisotropy may be crucial in determining the actual shapes of precipitates, even when the magnitude of such effects is relatively small. We know from Grabovsky's thesis work that anistropy favors sequential lamination. It is tempting to guess that surface energy favors cuboidal precipitates, but this is strictly conjecture.

2.2.3. The role of surface energy

(a) R. Kohn and S. Muller, "Surface energy and microstructure in coherent phase transitions," Comm. Pure Appl. Math. 47 (1994) 405-435.

A major success of the variational viewpoint is its ability to explain the crystallographic theory of martensite -- including, for example, the directions of twin and habit planes and the relative volume fractions of different phase variants. Fine scale features such as the length scale of twinning are not predicted by this theory however. It is widely believed that such details can be explained by including the effect of surface energy. Old though this idea is, its consequences have never been properly explored. The work of Kohn and Muller considers variational problems of the type $\iint [\phi_x^2 + (\phi_y^2 - 1)^2 + \varepsilon^2\phi_{yy}^2]\, dxdy$, where ϕ is scalar valued on the domain $0 < x < L$, $0 < y < 1$, with boundary condition $\phi = 0$ at $x = 0$. It models the main features of an austenite-twinned martensite interface, as Kohn and Muller showed in [27]. The function ϕ is the amplitude of the shear due to phase transformation; the sets where $\phi_y \approx -1$ and $\phi_y \approx 1$ are the twins; $x = 0$ is the approximate interface; and the "strain gradient" term $\varepsilon^2\phi_{yy}^2$ assigns surface energy of order ε to the twin boundaries. The analysis of Kohn and Muller shows that the minimum value of the energy is of order $\varepsilon^{2/3}L^{1/3}$. It also gives evidence that the minimizers must branch self-similarly near $x = 0$ as $\varepsilon \to 0$. This is one of very few cases where the effect of a strain gradient or surface energy perturbation to a nonconvex variational problem has been analyzed with full mathematical rigor. Materials scientists had missed the role of surface energy in promoting branching, though something similar had been noted in the context of ferroelastic domains [37].

2.2.4. Motion by weighted curvature

(a) P. Girao and R. Kohn, "Convergence of a crystalline algorithm for the heat equation in one dimension and for the motion of a graph by weighted curvature," Numer. Math. 67 (1994) 41-70.

This was part of Pedro Girao's thesis. There are many situations where elastic energy is unimportant and surface energy is dominant, see e.g. [20]. A natural evolution law in such settings is "motion by (weighted) curvature," which represents steepest descent with respect to (possibly anisotropic) surface energy. Girao's thesis considered a new numerical method known as "crystalline approximation." The idea is to approximate a smooth surface energy by a "crystalline one" -- one which prefers polygons rather than smooth surfaces -- then solve the analogous motion law for this approximate energy. Algorithms of this type have been implemented by several people, including Taylor [30], but a mathematical justification was lacking. The paper of Kohn and Girao provided such a justification for the simplest example: the motion of a graph in the plane. Girao also wrote a second paper, justifying the method for simple, closed, convex curves in the plane. When specialized to graphs, the crystalline approximation becomes something like a Galerkin scheme. When specialized to convex plane curves and presented in the proper variables, it resembles instead a finite difference scheme. This work established convergence in appropriate norms, with an explicit rate that depends on the number of tangent directions permitted in the discretized problem.

2.3. SMART MATERIALS

Smart materials are those whose physical properties are *controllable,* e.g. by applying a stress or changing the temperature. Shape-memory materials provide a particular, technologically important example. The source of their special properties is a martensitic phase transformation. Though a heuristic explanation of shape-memory behavior has been available for many years, our micromechanical understanding of this effect is still far from complete. Actually, there is not just a single "shape-memory" effect: the phenomenology of these materials is complicated, with effects such as recoverable strain, pseudoelastic hysteresis, rubber-like behavior, etc. occurring in different materials or at different temperatures.

2.3.1. Shape-memory polycrystals

(a) K. Bhattacharya and R. Kohn, "Symmetry, texture, and the recoverable strain of shape-memory polycrystals," to appear in Acta Metall. Mater.

Bhattacharya and Kohn have been modelling the effective behavior of shape memory polycrystals. These materials have the ability to recover, on heating, apparently plastic deformation. Some alloys have excellent shape memory as single crystals but little or none as polycrystals; others, including the technologically important TiNi, display good shape memory behavior even as polycrystals. The work of Kohn and Bhattacharya aims to explain the difference, by modelling how the recoverable strain of a polycrystal depends on its texture and the symmetry of the underlying martensitic phase transformation. The essential

mechanism of shape memory is well understood: deformation is recoverable because it is due not to slip, but to rearrangement of martensite variants. Since shape memory in single crystals can be analyzed via elastic energy minimization, the study of shape memory polycrystals is a problem in nonlinear homogenization. There is an easy estimate for the recoverable strain of a polycrystal, analogous to "Taylor's hypothesis" in plasticity. It suggests that crystals with few variants of martensite (associated, for example, with cubic to tetragonal or trigonal phase transformations) should lose their shape memory behavior in polycrystalline form, while crystals with many variants of martensite (e.g. those with orthorhombic or monoclinic martensite) should keep their shape memory behavior as polycrystals. This prediction is consistent with experimental observations, and it has been made before, albeit in a less quantitive way [31]. The paper (a) explores the Taylor estimate and its consequences. Bhattacharya and Kohn have also been investigating the accuracy of the Taylor hypothesis through a variety of examples, model problems, and rigorous bounds. These results are being prepared for separate publication.

2.3.2. Rubber-like behavior and slowly relaxing shifts

(a) K. Bhattacharya, R. James, and P. Swart, "A nonlinear dynamic model for twin relaxation with applications to Au-47.5at.%Cd and other shape-memory alloys," in Twinning in Advanced Materials (M.H. Yoo, ed.), The Materials Society, 1994

(b) K. Bhattacharya, R. James, and P. Swart, in preparation.

Bhattacharya and Swart have been working with R. James to model the ''rubber-like behavior'' displayed by certain shape-memory alloys in the martensite phase. Examples of such materials include AuCd (extensively studied in [32]), and also AuCuZn, InTl, InPb, and CuZnAl. In these materials, a twinned specimen can easily be detwinned by loading. If the loads are released soon after detwinning, the specimen spontaneously returns to the original twinned configuration. If the loads are held for some time after detwinning, however, the specimen remains detwinned even after the loads are released. This memory effect -- which is different from the classical shape memory effect -- is even more striking when periodic loading is applied to the specimen. The resulting stress-strain hysteresis loops are observed to slowly stabilize to a terminal loop characteristic of the material, the cycling frequency, and the temperature. The origin of this behavior is controversial, but one suggestion has been transient shuffle-twinning with slowly relaxing shifts. Papers (a)-(b) provide the first quantitative exploration of this idea. This problem turns out to be remarkably subtle mathematically. It makes a great deal of difference how one handles the nucleation of new twins and the kinetics of phase boundaries. There are strong links to optimal control theory and dynamical systems. Numerical simulation has been a crucial element of this work, both as a tool for determining the behavior of the model and as a source of conjectures for analytical attention.

2.4. OSCILLATORY SOLUTIONS OF EVOLUTION EQUATIONS

Our research is concerned with physical problems where the quantities of interest are oscillatory. In situations such as turbulent flow, it is not sufficient to consider statics: one must work with evolution equations instead. In some settings the physically relevant oscillations are due to randomness in the initial data.

2.4.1. Turbulent transport

(a) M. Avellaneda and A. Majda, "Simple examples with features of renormalization for turbulent transport," Phil. Trans. Roy. Soc. Lon. 346A (1994) 205-233

(b) M. Avellaneda and A. Majda, "Superdiffusion in nearly stratified flows," J. Stat. Phys. 69 (1992) 689-729

(c) C. Apelian, M. Avellaneda, and F. Elliott, "Trapping, percolation, and anomalous diffusion of particles in a two-dimensional random field," J. Stat. Phys. 72 (1993) 1227-1304

(d) M. Avellaneda and M. Vergassola, "Stieltjes integral representation for the effective diffusivity of a passive scalar in a time-dependent incompressible flow," submitted to Phys. Rev. E

Papers (a) and (b) continue the program of Avellaneda and Majda, using methods from homogenization and the theory of stochastic processes to study the passive advection of a scalar quantity by a stationary, incompressible velocity field. The basic equation is $\frac{\partial T}{\partial t} + u \cdot \nabla T = D_0 \Delta T$, $T(x,0) = T_0(\varepsilon x)$. The velocity field u is assumed to be random, so the solution T is random as well. The goal is to understand, in terms of the structure of u, the limiting behavior of T in the long-time, large-distance limit. The content of (a) is a family of illustrative examples. Most work in this area considers ‘‘stratified’’ flow fields, i.e. velocity fields u with only one nonzero component. The paper (b) goes further, obtaining analytical results for flow fields which are only *nearly* stratified.

The paper (c) reflects Chris Apelian's thesis work. It addresses the case of molecular diffusivity $D_0 = 0$. In this case the basic equation $T_t + u \cdot \nabla T = 0$ becomes a first-order PDE. Solving it by the method of characteristics amounts to considering a certain stochastic differential equation describing particle trajectories $x(t)$. The goal, as always, is to understand the long-time/large-scale behavior -- in other words, to identify the overall rate at which particles are transported. In particular, one wants to know the exponent ν such that $< |x(t) - <x(t)>|^2 > \,\simeq t^{\nu}$. The effective behavior is ‘‘diffusive’’ if ν=1, and ‘‘superdiffusive’’ if ν>1. The work of Avellaneda, Apelian, and Elliott provides what is perhaps the first fully non-stratified example to be thoroughly understood. They consider velocity fields of the form $u = (u_1(x_2), u_2(x_1))$. Using Monte Carlo techniques to solve the underlying stochastic differential equations numerically, they obtain numerical results on the effective behavior. At one extreme is the case when the mean velocity is zero. Then all stream lines turn out to get trapped, and there is no effective diffusion. At the other extreme is the case when the mean velocity is sufficiently large. This case is exactly

solvable, and the effective behavior is diffusive. The intermediate case, when the mean velocity is of moderate size, was explored in detail as well.

All the preceding work considered stationary, divergence-free velocity fields $u(x)$. In (d), Avellaneda and Vergassola consider the effective diffusivity problem for *time-dependent* divergence-free flow. Their main result is a Stieltjes representation formula for the effective diffusivity and its dependence on u. Aside from some recent work of Fannjiang and Papanicolaou, this is basically the first analytical progress concerning the effective diffusivity associated with time-dependent velocity fields. The analogous integral representation for stationary flows was obtained by Avellaneda and Majda in 1988. The work of Avellaneda and Vergassola has implications for the transport of passive scalars in Navier-Stokes turbulence, and for the enstrophy dissipation rate in 2D turbulence. The Stieltjes representation can be used to resum the (divergent) perturbation series for the dissipation rate in terms of the Peclet or Reynolds number. Avellaneda is presently investigating applications of this representation formula to 2D turbulence, with PhD student Yingzi Zhu.

2.4.2. Random solutions of Burgers' equation

(a) M. Avellaneda and Weinan E. "Statistics of shocks in Burgers turbulence," to appear in Comm. Math. Phys.

(b) M. Avellaneda, "Statistics of shocks in Burgers Turbulence II: tail probabilities for velocities, shock-strengths, and rarefaction intervals," to appear in Comm. Math. Phys.

(c) M. Avellaneda, Weinan E, and R. Ryan, "Probability distrubution functions for velocity and velocity gradients in Burgers turbulence," submitted to Phys. Fluids

Weinan E was our ARO-sponsored postdoc from 1989 to 1991. His subsequent position was at the Institute for Advanced Study in Princeton. We are delighted to say that Weinan joined the faculty of the Courant Institute in September, 1994 as a tenured Associate Professor.

The work by Avellaneda and E, reported in (a) and (b), was begun during E's final months as a postdoc in 1991. It concerns Burgers' equation $u_t + u \cdot \nabla u = 0$ with "white noise" initial data. Burgers proposed this problem long ago as a simplified model for hydrodynamical turbulence. By now we know that Burgers' equation is not a good model for turbulence, since it lacks crucial mechanisms such as vortex stretching. But it remains important for other reasons. One application is to cosmology, where the "adhesion model" of Zeldovich models how matter forms into clusters (galaxies) through gravitational interaction [33]. Most work in this area has been done by the physics community, based largely on numerical simulation. But an exact solution formula for Burgers' equation is available, through the Hopf-Cole transformation and the work of Peter Lax. When the initial data is random this representation is not easy to use -- but that is what Avellaneda and E achieved. The result is a lot of rigorous and detailed statistical information, including probability distribution of very strong and very weak shocks.

Avellaneda's Ph.D. student Reade Ryan is working in this area, and (c) represents part of his thesis work. It extends the analysis of (a)-(b) to the case of nonzero viscosity, using the Hopf-Cole transformation.

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3. STUDENTS

The following 5 Ph.D. students completed theses in areas related to our ARO-sponsored research during the term of this contract:

Karen Clark (August, 1992)

Advisor: Graeme Milton

Thesis: "Characterizing the possible conductivity functions of composite materials"

First job: Assistant Professor, University of Michigan

Research: See Sections 2.1.1 and 2.1.2

Pedro Girao (January 1993)

Advisor: Robert Kohn

Thesis: "Convergence of a crystalline algorithm for motion by weighted curvature"

First job: Assistant Professor, Technical University of Lisbon

Research: See Section 2.2.4

Jiangbo Lu (July, 1993)

Advisor: Robert Kohn

Thesis: "Elastic energy minimization and the shapes of coherent precipitates"

First job: Postdoctoral position, Carnegie Mellon University

Research: See Section 2.2.2

Christopher Apelian (July, 1993)

Advisor: Marco Avellaneda

Thesis: "Anomalous diffusion and percolation results for transport in a two-dimensional random field"

First job: Assistant Professor, Drew University.

Research: See Section 2.4.1

Yury Grabovsky (June, 1994)

Advisor: Robert Kohn

Thesis: "Bounds and extremal microstructures for two-component composites: a unified treatment based on the translation method"

First job: Postdoctoral position, Carnegie Mellon University, on leave from University of Utah

Research: See Section 2.1.4

We are currently supervising the research of four more students:

Reade Ryan (expected to finish summer, 1996)

Advisor: Marco Avellaneda

Research: Random solutions of Burgers' equation.

Weimin Jin (expected to finish summer, 1996)

Advisor: Robert Kohn

Research: Minimization of elastic + bending energy, as proposed by Gioia and Ortiz for modelling the detachment of certain thin films.

Yingzhi Zhu (expected to finish summer, 1996)

Advisor: Marco Avellaneda

Research: Turbulent transport.

Matthew Killough (now in his second year of graduate study)

Advisor: Robert Kohn

Research: Now preparing for the Oral Comprehensive Exams; will choose a thesis topic in fall, 1995.

4. LIST OF PUBLICATIONS SUPPORTED BY THIS CONTRACT

This contract generated 34 research articles published in or submitted to refereed journals, and another 12 contributions to conference proceedings volumes. We list them alphabetically by author.

Articles in refereed journals:

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13. ABSTRACT (Maximum 200 words)
This is the final technical report on ARO contract DAAL03-92-G-0011, which began February 1, 1992 and ended January 31, 1995. The scientific focus of this project lies at the frontier where mathematics meets materials science. We are concerned with the effective moduli of composites, the formation of microstructure in coherent phase transitions, and the random solutions of nonlinear evolution equations. These diverse problems are linked by a common theme: the relationship between microstructure and macroscopic behavior. Our achievements under this contract include: (i) development of a theory for how symmetry and texture determine the recoverable strain of a shape-memory polycrystal; (ii) development of a model for piezoceramic composites, providing insight toward the design of such materials for use in sensors or actuators; and (iii) new, optimal bounds on the effective behavior of elastic polycrystals. The training of young scientists has been a major part of our activity.

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